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(54) **Elastomer composition which contains intercalated and exfoliated clay reinforcement formed in situ within the elastomer host and article, such as a tire, having at least one component thereof**

(57) This invention relates to a rubber composition which contains intercalated and at least partially exfoliated organophilic clay reinforcement formed in situ within the elastomer host from a hydrophilic clay. The invention particularly relates to an in situ modification of a hydrophilic clay to compatibilize the clay with a diene-based elastomer. The clay is converted from being hydrophilic in nature to being more hydrophobic in nature and therefore more compatible with the elastomer by bulk blending the elastomer host with a smectite clay, preferably a montmorillonite or hectorite clay, and a hydrocarbyl onium salt, such as for example a quaternary ammonium salt, and particularly in the absence of water

addition to the elastomer host. Therefore, such in situ procedure of intercalation and at least partially exfoliation relies upon a bulk blending thereof with an elastomer host at an elevated temperature and under high shear conditions in contrast to pre-intercalating the clay in an aqueous based medium and in contrast to simple low viscosity melt processing of a thermoplastic polymer. The invention also relates to articles of manufacture, including tires, having at least one component comprised of such rubber composition. Such tire component may be, for example, a tire tread.

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**Description**Field of the Invention

5 [0001] This invention relates to a rubber composition which contains intercalated and at least partially exfoliated organophilic clay reinforcement formed in situ within the elastomer host from a hydrophilic clay. The invention particularly relates to an in situ modification of a hydrophilic clay to compatibilize the clay with a diene-based elastomer. The clay is converted from being hydrophilic in nature to being more hydrophobic in nature and therefore more compatible with the elastomer by bulk blending the elastomer host with a smectite clay, preferably a montmorillonite or hectorite  
10 clay, and a hydrocarbyl onium salt, such as for example a quaternary ammonium salt, and particularly in the absence of water addition to the elastomer host. Therefore, such in situ procedure of intercalation and at least partially exfoliation relies upon a bulk blending thereof with an elastomer host at an elevated temperature and under high shear conditions in contrast to pre-intercalating the clay in an aqueous based medium and in contrast to simple low viscosity melt processing of a thermoplastic polymer. The invention also relates to articles of manufacture, including tires, having at  
15 least one component comprised of such rubber composition. Such tire component may be, for example, a tire tread.

Background of the Invention

20 [0002] Various natural occurring clays may be blended with various elastomers which usually act as relatively inactive fillers in rubber compositions insofar as reinforcement of the rubber compositions is concerned. Representative of such clays are, in general, for example, bentonite and kaolin clays. Such clays are conventionally hydrophilic in nature and therefore are relatively incompatible with diene-based elastomers.

25 [0003] However, some clays, such as, for example, smectite clays, and particularly montmorillonite clays which might be considered to be in a nature of a species of a bentonite clay, can be changed from being hydrophilic in nature to a clay being hydrophobic in nature and therefore more compatible with diene-based elastomers.

[0004] From an historical perspective, some naturally occurring layered clay minerals such as, for example, montmorillonite clay, which are hydrophilic in nature, are composed of a plurality of platelets which have a tendency to swell in the presence of water as a result of an associated increase of the distance between the platelets.

30 [0005] Such clay, particularly a montmorillonite clay, may be intercalated by chemical ion exchange methods. For such intercalation of a montmorillonite clay, the clay may be immersed in water to cause the clay to swell and a quaternary ammonium salt introduced, or included, in the water to cause the typically occurring sodium ions in the space between the platelets to be exchanged with the quaternary ammonium ion from the quaternary ammonium salt to further expand the distance between the platelets and to thereby intercalate the clay. If an alkyl quaternary ammonium salt is used which can impart aliphatic hydrocarbon chains on the surface of the clay by the ion exchange process, the intercalated clay can become more hydrophobic in nature and therefore more compatible with elastomers, particularly with diene-based elastomers.

35 [0006] The intercalated clay may then be dried and blended with an elastomer(s) under conditions of elevated temperature and relatively high shear conditions to cause the swelled and intercalated clay to at least partially exfoliate, or separate into small, individual platelets within the rubber composition and to contribute to the reinforcement of the rubber composition itself. Such intercalation procedure for montmorillonite clay and use thereof for reinforcement of rubber compositions is well known to those having skill in such art.

40 [0007] For example, an intercalated clay might be historically prepared by obtaining a smectite clay, other than a kaolin type clay, namely a clay such as, for example, a montmorillonite clay, which is comprised of a plurality of stacked layers, or platelets and which is swellable upon dispersion in water; dispersing the clay in an aqueous solution of a surfactant (e.g. a quaternary ammonium salt) which causes the clay to swell so that the average spacing between the platelets typically expands from 4 Angstroms to an average spacing in a range of 10 to 30 Angstroms; followed by drying the treated, or intercalated, clay.

45 [0008] The smectite clay (e.g. montmorillonite clay) for use in this invention contains sodium ions between its layered platelets and the larger surfactant molecules contained in the water solution in which the clay is immersed position themselves between the layered platelets by an ion exchange with the sodium ions to cause or otherwise enhance the separation of the platelets to make the platelets more amenable to subsequent exfoliation.

50 [0009] Hydrophilic clays typically have a relatively high concentration of oxygen on their exposed surfaces and are therefore relatively incompatible with diene-based elastomers.

55 [0010] It is therefore often desirable to create intercalated clays which are more hydrophobic in nature by forming a predominance of aliphatic hydrocarbon chains on its exposed surfaces, thereby causing the intercalated clay to be more hydrophobic in nature. Such converted intercalated clays having aliphatic hydrocarbon chains on their surface are sometimes referred to as organoclays or might be sometimes as organophilic clays.

[0011] As hereinbefore related, the formation of aliphatic hydrocarbon chains on the surfaces of intercalated clay,

and associated exfoliated platelets thereof may be accomplished, for example, by utilization of alkyl quaternary ammonium salts for treatment of the clay in its aqueous dispersion to create organoclays which are hydrophobic in nature which are more compatible with diene-based elastomers and therefore more readily dispersible in such elastomeric compositions.

5 [0012] Such conversion of naturally occurring hydrophilic clays such as montmorillonite clay to more hydrophobic organoclays for a more suitable dispersion in various elastomers is well known to those having skill in such art.

[0013] However, such operational steps to create more useful organoclays of a hydrophobic nature, including associated intercalated clays and exfoliated clay platelets for reinforcement of rubber composition, are process intensive. This is because of the aforesaid considerable and involved sequential steps of, for example, first immersing the hydrophilic clay in water which contains, for example, a suitable quaternary ammonium salt to cause it to swell and intercalate with an associated conversion of the clay to a hydrophobic organoclay, drying the organoclay, followed by dispersing the intercalated organoclay within an elastomer under high sheer mixing conditions to cause the intercalated organoclay to at least partially exfoliate into a plurality of individual platelets.

10 [0014] Accordingly, it is desired to enhance a creation of an intercalated and exfoliated montmorillonite clay which is hydrophobic in nature for use in the reinforcement of rubber compositions.

[0015] Historically, blending of an organoclay with a thermoplastic or thermosetting polymer by a melt blending process is discussed in US-A-4,739,007; 4,810,734; 5,385,776; 5,578,672 and 5,840,796. Historically, blending of an adduct of a mineral filler such as for example a montmorillonite clay, and a quaternary ammonium salt with at least one rubber and an organosilane is discussed in US-A- 4,431,755.

15 [0016] For the description of this invention, the term "elastomer exfoliated nanoclay composite" means, unless otherwise indicated herein, an elastomer composition which contains an intercalated clay, in which the intercalated clay is at least partially exfoliated in situ within the elastomer host, particularly a smectite clay as a sodium montmorillonite clay, in which the particles are primarily organoclay platelets, and fragments of such platelets, wherein the platelets are somewhat circular and possibly elliptical in shape having an average, somewhat irregular, length and width, in a range of, for example, 100 to 1000 nanometers.

20 [0017] The smectite clay, preferably the montmorillonite clay, for use in this invention, might be described, for example, as a naturally occurring clay of a structure which is composed of a plurality of stacked, thin and relatively flat, layers, where such individual layers may be of a structure viewed as being composed of very thin octahedral shaped alumina layer sandwiched between two very thin tetrahedrally shaped silica layers to form an aluminosilicate structure.

25 [0018] Generally, for such aluminosilicate structure in the naturally occurring montmorillonite clay, some of the aluminum cations ( $\text{Al}^{+3}$ ) are viewed as having been replaced by magnesium cations ( $\text{Mg}^{+2}$ ) which results in a net negative charge to the platelet layers of the clay structure. Such negative charge is viewed as being balanced in the naturally occurring clay with hydrated sodium, lithium, magnesium, calcium and/or potassium cations within the spacing (sometimes referred to as "galleries") between the aforesaid aluminosilicate layers, or platelets. The average spacing, between the layers, or platelets, typically in a range of 1 to 5 Angstroms, is largely determined by the nature of such aforesaid cation residues contained with the spacing and by the degree of hydration and which may be measured by x-ray diffraction method.

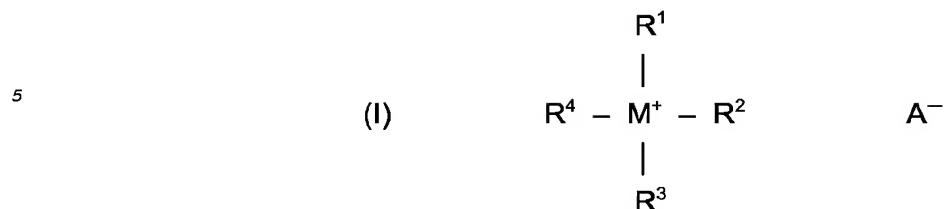
30 [0019] In the description of this invention, the term "phr" is used to designate parts by weight of a material per 100 parts by weight of elastomer. The terms "rubber" and "elastomer" may be used interchangeably unless otherwise indicated. The terms "vulcanized" and "cured" may be used interchangeably, as well as "unvulcanized" or "uncured", unless otherwise indicated.

#### Summary and Practice of the Invention

35 [0019] In accordance with this invention, a process of preparing a rubber composition which contains a dispersion of intercalated and at least partially exfoliated clay comprises blending, based upon parts by weight per 100 parts by weight rubber (phr):

- 50 A. 100 phr of at least one hydrocarbon diene-based elastomer,
- B. one to 20, alternately one to 6, phr of smectite clay, preferably montmorillonite and/or hectorite clay,
- C. a hydrocarbyl onium salt, and
- D. 20 to 99 phr of at least one additional reinforcing filler comprised of carbon black, synthetic amorphous silica or silica treated carbon black and mixtures thereof,

55 wherein said hydrocarbyl onium salt is of the general formula (I) represented in an ionized form comprised of a cation and an anion ( $\text{A}'^-$ ):



wherein R<sup>1</sup> is hydrogen or an alkyl group containing from one to three carbon atoms, such as, for example, methyl, ethyl, isopropyl and n-propyl groups; R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are individually selected from alkyl groups having from 15 one to 40, alternately from one to 18 carbon atoms and allyl and aryl groups having from 6 to 40, alternately from 6 to 18, carbon atoms; and

20 wherein A<sup>-</sup> is an anion selected from one of chloride, bromide, iodide, fluoride, cyanide, nitrate, hydroxide, thiocyanate, perchlorate, chlorate, bromate, permanganate, formate, acetate, propionate, benzoate, m-toluate, p-toluate, salicylate, methane sulfonate, bisulfate, bicarbonate, dihydrogen phosphate, phenoxide, picrate, methoxide, alkoxide and like anions having a single negative charge, preferably Cl<sup>-</sup>; and wherein M is selected from nitrogen, sulfur or phosphorous, preferably nitrogen.

[0020] Representative of such alkyl groups for the R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> group(s) are, for example straight chain groups such as, for example, methyl, octyl, decyl and octadecyl, groups, and branched chain groups such as, for example, an ethylhexyl group, as well as tallow (usually about 18 carbon atoms) and hydrogenated tallow.

[0021] Thus the hydrocarbyl onium salt may be, for example, an alkyl quaternary ammonium salt where such alkyl 25 quaternary ammonium ion is a cation and chlorine is an anion.

[0022] In practice, said hydrocarbyl onium salt is therefore typically a quaternary ammonium salt and typically used in an amount in a range of 0.5 to 2 moles of ammonium moiety of said salt per mole of sodium ion of said clay.

[0023] Representative examples of hydrocarbyl onium salts are exemplified in US-A- 2,531,396, and which exemplifies various amine based salts, ammonium compounds such as quaternary ammonium salts, pyridinium compounds 30 and phosphonium compounds.

[0024] Further representative examples are methyl trialkyl ammonium chloride, trimethyl alkyl ammonium chloride, dimethyl dialkyl ammonium chloride, dimethyl alkyl allyl ammonium chloride and dimethyl diallyl ammonium chloride.

[0025] In practice, for example, a methyl trialkyl quaternary ammonium salt, such as, for example, methyl trioctyl 35 quaternary ammonium salt is seen herein to undergo an ionic exchange with sodium ions contained on the surface of said montmorillonite clay, all in situ within the elastomer host and in the absence of a pre-swelling of the clay in an aqueous dispersion thereof, to replace at least a major portion of said sodium ions with the alkyl quaternary ammonium salt to thereby cause the montmorillonite clay to become more hydrophobic nature and thus more compatible with the elastomer host.

[0026] While particulate carbon black and amorphous silica, and sometimes clay, have heretofore been used for 40 reinforcing rubber compositions for various tire components, a tire with certain component(s) comprised of a rubber composition which contains an intercalated organoclay which is both intercalated and exfoliated in situ by bulk blending within the elastomer host at elevated temperature and under high shear conditions is considered herein to be novel and a significant departure from past practice.

[0027] In further accordance with this invention, said rubber composition is provided wherein said montmorillonite 45 clay is intercalated and at least partially exfoliated and, also rendered more hydrophobic in nature, all in situ within said elastomer host, wherein said exfoliated platelets are relatively thin, two dimensional platelets homogeneously dispersed with the elastomer host.

[0028] In additional accordance with this invention, said rubber composition is provided wherein said intercalated 50 and exfoliated montmorillonite clay is in a form of organophilic platelets having a thickness in a range of one to 20 nanometers (nm), a length in a range of 50 to 500 nm and an aspect ratio (length to thickness) in a range of from 50/1 to 500/1

[0029] A significant aspect of this invention is the generation of an organoclay in situ within the elastomer host during the processing of the elastomer(s) which is considered herein to be a more efficient way of both hydrophobating and dispersing the clay within the elastomer host, all in the absence of a pre-intercalation of the clay and exclusive of a 55 pre-swelling of the clay in an aqueous dispersion thereof.

[0030] While the resultant invention appears to be relatively simplistic, such simplistic nature goes to the heart of the invention because it is considered herein that there is a sufficient complexity that the essence of the invention involving application of an ion exchange mechanism, normally required to include treatment of a clay by a pre-swelling of the

clay in an aqueous dispersion, which can only be determined by an appropriate experimentation and trial, especially in view of the aforesaid prior practice of first both swelling and pre-treating the clay in an aqueous medium, recovering and drying the treated clay followed by mixing the recovered, treated clay with one or more elastomers to cause the treated clay to at least partially exfoliate within the elastomer.

5 [0031] In further accordance with this invention, a rubber composition is provided which has been prepared by such method.

[0032] In additional accordance with this invention, an article of manufacture is provided having at least one component comprised of the rubber composition of this invention.

10 [0033] In further accordance with this invention, a tire is provided having at least one component comprised of the rubber composition of this invention.

[0034] In additional accordance with this invention, a tire having a tread comprised of the rubber composition of this invention is provided.

[0035] In practice, a coupling agent may also be used to aid in coupling said hydrophobic intercalated clay particles and exfoliated platelets thereof, as the case may be, to an associated diene-based elastomer host.

15 [0036] Preferably such coupling agent is mixed with the elastomer subsequent to the intercalation, and preferably after the at least partial exfoliation or at least after a major extent of the partial exfoliation of the clay (e.g. after at least 50 percent of said partial exfoliation) so that the coupling agent does not interfere with the clay's intercalation, and preferably does not unnecessarily interfere with said at least partial exfoliation, as well as transformation of the clay from its inherent hydrophilic nature to a more hydrophobic nature.

20 [0037] Such coupling agents typically have a moiety which is reactive with hydroxyl groups (which might be silanol groups) contained on the surface of the intercalated clay and exfoliated platelets, as the case may be, and another moiety interactive with at least one of said elastomers.

[0038] For example, although not intended to be limiting, such coupling agents may include, for example, bis(3-alkoxysilylalkyl) polysulfides, such as, for example, a bis(3-alkoxysilylpropyl) polysulfide having an average of from 2 to 2.6 or from 3.5 to 4, connecting sulfur atoms in its polysulfidic bridge. Bis(3-ethoxysilylpropyl) polysulfides may be preferred.

25 [0039] For this invention, said exfoliated montmorillonite clay platelets are viewed herein as being in a form of thin, substantially two dimensionally shaped materials in a sense that their planar length and width dimensions are in a range of 50 to 2000 nanometers for said particles of stacked platelets and 50 to 500 nanometers for said exfoliated platelets, with the length being longer than the width, and with a thickness in a range of 10 to 40 nanometers for said particles of stacked platelets and about one nanometer for said exfoliated platelets.

30 [0040] In practice, for the purposes of this invention, the montmorillonite clay is homogeneously dispersed in and is intercalated and at least partially exfoliated as well as being rendered more hydrophobic in nature, all in situ within its elastomer host, by mixing said clay, in the absence of water, with said diene-based elastomer(s) at a temperature in a range of 100°C to 175°C and under conditions sufficient to intercalate, and at partially exfoliate, said clay in an internal mixer in combination with a quaternary ammonium salt of the general formula (I).

35 [0041] In practice, it is considered herein that the montmorillonite clay becomes more compatible with the diene-based elastomer host after its intercalation and exfoliation as well as its transition to a more hydrophobic form, all in situ within the elastomer host.

40 [0042] For such combination of intercalation and exfoliation of the clay, as well as its transformation to a more hydrophobic form, all within the elastomer host at the elevated temperature, it is preferred that 30 to 95, alternately 30 to 60 or alternately 60 to 95, weight percent of the intercalated clay becomes intercalated and, at least to some extent exfoliated, within the elastomer host during the mixing thereof.

45 [0043] In practice, various diene-based elastomers may be used for the tire component (e.g. tire tread) such as, for example, homopolymers and copolymers of monomers selected from isoprene and 1,3-butadiene and copolymers of at least one diene selected from isoprene and 1,3-butadiene and a vinyl aromatic compound selected from styrene and alphamethyl styrene, preferably styrene.

50 [0044] Representative of such conjugated diene-based elastomers are, for example, cis 1,4-polyisoprene (natural and synthetic), cis 1,4-polybutadiene, styrene/butadiene copolymers (aqueous emulsion polymerization prepared and organic solvent solution polymerization prepared), medium vinyl polybutadiene having a vinyl 1,2-content in a range of 15 to 90 percent, isoprene/butadiene copolymers, styrene/ isoprene/butadiene terpolymers. Tin coupled elastomers may also be used, such as, for example, tin coupled organic solution polymerization prepared styrene/butadiene copolymers, isoprene/butadiene copolymers, styrene/isoprene copolymers, polybutadiene and styrene/isoprene/butadiene terpolymers.

55 [0045] In the practice of this invention, where natural rubber is to be used, the grade of purity of cis 1,4-polyisoprene natural rubber is preferred to be of quality, or grade, of Rib Smoked Sheet Number 2 (R.S.S.#2) or better, according to The Green Book of the IRQPC (International Standards of Quality and Packing of Natural Rubber Grades).

[0046] In the further practice of this invention, particulate reinforcement for the rubber composition may also include particulate synthetic amorphous silica, particularly precipitated silica, or a combination of carbon black and amorphous

silica (exclusive of silica treated carbon black), usually of an amount in a range of 35 to 100 alternately 35 to 90, phr. If a combination of such carbon black and silica is used, usually at least 5 phr of carbon black and at least 10 phr of silica are used. For example, a weight ratio of silica to carbon black ranging from 1/5 to 5/1 might be used.

[0047] Commonly employed synthetic amorphous silica, or siliceous pigments, used in rubber compounding applications can be used as the silica in this invention, including precipitated siliceous pigments and fumed (pyrogenic) silica wherein aggregates of precipitated silicas are usually preferred.

[0048] The precipitated silica aggregates preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate and may include coprecipitated silica and a minor amount of aluminum.

[0049] Such silicas might usually be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of 40 to 600, and more usually in a range of 50 to 300 square meters per gram. The BET method of measuring surface area is described in the Journal of the American Chemical Society, Volume 60, Page 304 (1930).

[0050] The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of 50 to 400 cm<sup>3</sup>/100g, and more usually 100 to 300 cm<sup>3</sup>/100g.

[0051] Various commercially available precipitated silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas from PPG Industries under the Hi-Sil trademark with designations Hi-Sil 210, Hi-Sil 243, etc; silicas from Rhodia as, for example, Zeosil 1165MP and Zeosil 165GR, silicas from Degussa AG with, for example, designations VN2 and VN3, as well as other grades of silica, particularly precipitated silicas, which can be used for elastomer reinforcement.

[0052] As hereinbefore discussed, various coupling agents may be used if desired. For example, a bis(3-trialkoxysilylalkyl) polysulfide having an average of 2 to 2.6 or of 3.5 to 4 connecting sulfur atoms in its polysulfide bridge may be used.

[0053] It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts.

[0054] Typical amounts of tackifier resins, if used, comprise 0.5 to 10 phr, usually 1 to 5 phr. Typical amounts of processing aids comprise 1 to 50 phr. Such processing aids can include, for example, aromatic, napthenic, and/or paraffinic processing oils. Typical amounts of antioxidants comprise 1 to 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in The Vanderbilt Rubber Handbook (1978), Pages 344 through 346. Typical amounts of antiozonants comprise 1 to 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise 0.5 to 3 phr. Typical amounts of zinc oxide comprise 1 to 10 phr. Typical amounts of waxes comprise 1 to 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise 0.1 to 1 phr.

[0055] The vulcanization is conducted in the presence of a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur vulcanizing agents are used in an amount ranging from 0.5 to 4 phr, or even, in some circumstances, up to 8 phr.

[0056] Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally and preferably, a primary accelerator(s) is used in total amounts ranging from 0.5 to 4, preferably 0.8 to 1.5, phr. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in smaller amounts (of 0.05 to 3 phr) in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators might be expected to produce a synergistic effect on the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

[0057] The presence and relative amounts of the above additives are not considered to be an aspect of the present invention, unless otherwise indicated herein, which is more primarily directed to the utilization of a particulate reinforce-

ment of a conjugated diene-based elastomer for a component of a tire (e.g. tire tread) prepared by in situ intercalation and partial exfoliation of the clay within the elastomer host.

**[0058]** The mixing of the rubber composition can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages, namely, at least one non-productive stage followed by a productive mix stage. The final curatives are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber, and fillers such as silica and silica treated carbon black and adhesive agent, are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art.

**[0059]** The following examples are presented to illustrate the invention and are not intended to be limiting. The parts and percentages are by weight unless otherwise designated.

#### EXAMPLE I

**[0060]** A series of natural cis 1,4-polyisoprene rubber based compositions were prepared which are referred to herein as Samples A through F, with Samples A and B, as well as Sample F, being Control Samples.

**[0061]** Control Sample A is prepared without an addition of clay.

**[0062]** Control Sample B is prepared with an addition of non-intercalated montmorillonite clay.

**[0063]** Samples C, D and E are prepared in which 3.3, 6.6 and 3.3 phr, respectively, of an non-intercalated montmorillonite clay is added together with a methyl trialkyl quaternary ammonium salt so that the clay is both intercalated and partially exfoliated in situ with in the elastomer host.

**[0064]** Sample E is a duplicate of Sample C except that a reduced amount of carbon black reinforcement is used, namely 40 phr instead of 55 phr of carbon black.

**[0065]** Control Sample F is a duplicate of Control Sample A except that 5 phr of an organo clay, namely a pre-intercalated montmorillonite clay, was added to the rubber composition. No additional quaternary ammonium salt was added. The amount of 5 phr was used for the organo clay as a quantity similar to the sum of clay and quaternary ammonium salt (5 phr) used for Samples C and E. The organo clay for Control Sample F had been prepared by pre-intercalating montmorillonite clay with a quaternary ammonium salt prior to its addition to the rubber composition.

**[0066]** For this Example, in what is usually referred to as a non-productive mixing procedure, samples are prepared by first adding the natural rubber to an internal rubber mixer which had been preheated to a temperature of about 100°C and first mixing the rubber therein for about 30 seconds minutes to slightly break down the rubber and reduce its viscosity, following which the clay, where applicable, and other indicated ingredients, except for sulfur and associated sulfur vulcanization accelerators, are mixed with the elastomer for a total mixing time of about six minutes, to a temperature of about 160°C, after which the mixture is removed from the rubber mixer, open roll milled, sheeted out and cooled to a temperature below 40°C.

**[0067]** In what is usually referred to a subsequent mixing step, usually referred to as a productive mixing step, the mixture is introduced into an internal rubber mixer and sulfur and vulcanization accelerators are added and mixed for about three minutes to a temperature of about 100°C.

**[0068]** For this Example some degree of intercalation and at least partial exfoliation of the clay of Samples C, D and E occurs within the elastomer host, as well as a conversion of the hydrophilic nature of the clay to a more hydrophobic form due to the aforesaid ion exchange of alkyl group(s) of the said quaternary ammonium salt with sodium ions of the clay, so that a relatively homogeneous dispersion of the intercalated clay, delaminated clay platelets, and particles thereof, within the elastomer composition is obtained.

**[0069]** The compositions of Samples A through F are shown in the following Table 1.

Table 1

	Parts					
	Control	Control				Control
Material	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
<u>Non-Productive Mixing</u>						
Natural rubber <sup>1</sup>	100	100	100	100	100	100

<sup>1</sup>Cis 1,4-polyisoprene natural rubber of grade TSR-CV (Technical Specification Rubber, Constant Viscosity) which is understood to be of a grade equal to or better than R.S.S.#2 natural rubber

Table 1 (continued)

	Parts					
	Control	Control				Control
Material	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
<u>Non-Productive Mixing</u>						
Carbon black <sup>2</sup>	55	55	55	55	40	55
Processing oil <sup>3</sup>	3	3	3	3	3	3
Tackifying resin	2	2	2	2	2	2
Zinc oxide	2	2	2	2	2	2
Clay <sup>4</sup>	0	3.3	3.3	6.6	3.3	0
Quaternary ammonium salt <sup>5</sup>	0	0	1.7	3.4	1.7	0
Organic clay <sup>6</sup>	0	0	0	0	0	5
<u>Productive Mixing Step</u>						
Accelerator(s) <sup>7</sup>	1.6	1.6	1.6	1.6	1.6	1.6
Sulfur	5.5	5	5	5	5	5
Prevulcanization inhibitor <sup>8</sup>	0.3	0.3	0.3	0.3	0.3	0.3
Zinc oxide	3	3	3	3	3	3

2N326, an ASTM designation

3Naphthenic type rubber processing oil

4Montmorillonite clay, not intercalated, having an average spacing between its layers, or platelets, of about 4 Angstroms and obtained as Clarite NA+ from the Southern Clay Products Company.

5Methyl trialkyl quaternary ammonium salt obtained as Adogen® 464, a methyl trialkyl ammonium chloride, where said alkyl groups averaged from 8 to 10 carbon atoms, from the Aldrich Chemical Company

6Organic clay as a pre-intercalated clay of a hydrophobic nature obtained as Cloisite® 25A from Southern Clay Products

7Of the sulfonamide type

8Of the phthalimide type

[0070] Various physical properties of the Samples of Table 1 were evaluated and reported in the following Table 2.  
 [0071] In the following Table 2 the terms "UTS" and "RPA" mean "Ultimate Tensile System" and "Rubber Processability Analyzer", respectively.

Table 2

	Control	Control				Control
Properties	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
<u>UTS Determined Modulus/Tensile/Elongation</u>						
100% Modulus, MPa	4.5	4.4	7.8	9.2	5.5	6.9
150% Modulus, MPa	7.4	7	11.7	11.9	8.4	10.5
200% Modulus, MPa	10.8	10.2	15.5	--- <sup>3</sup>	11.8	14.3

<sup>3</sup>These values could not be determined because of early failure as can be seen by the corresponding ultimate elongation values.

Table 2 (continued)

	Control	Control				Control
Properties	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
<u>UTS Determined Modulus/Tensile/Elongation</u>						
300% Modulus, MPa	17.9	16.8	---3	---3	18.67	---3
Ult Tensile strength, MPa	22.1	20.9	17.6	12.5	23.7	19.6
Ult elongation (%)	372	378	234	174	378	284
<u>RPA at 100°C, 11 Hertz</u>						
G' at 1% strain (kPa) <sup>1</sup>	4086	3161	7752	8580	5052	5488
G' at 10% strain (kPa) <sup>1</sup>	2071	1778	3483	4168	2660	3013
Tan Delta at 1% strain <sup>2</sup>	0.11	0.11	0.09	0.08	0.06	0.07
Tan Delta at 10% strain <sup>2</sup>	0.15	0.15	0.15	0.15	0.12	0.11

1 The G' value at one percent strain, or elongation, namely a measure of Storage Modulus, as is well known to those having skill in such art, is considered herein to be a measure of stiffness, wherein an increase of G' is a corresponding indication of an increase in stiffness of the rubber composition.

2 The Tan Delta at one percent strain, or elongation, namely a ratio of Loss Modulus to Storage Modulus, as is well known to those having skill in such art, is considered herein to be a measure of hysteresis wherein a lower hysteresis is desirable for better tire rolling resistance (less resistance to rolling) and therefore better associated vehicular fuel economy. A decrease in the Tan Delta value is a corresponding indication of a decrease in hysteresis of the rubber composition.

3 These values could not be determined because of early failure as can be seen by the corresponding ultimate elongation values.

[0072] It can be seen from Table 2 that Samples C, D and E, which contain the in situ formed organoclay, namely the intercalated and partially exfoliated montmorillonite clay formed in situ within the elastomer host without a pre-intercalation of the clay in a water based medium, have a significantly increased G', and therefore increased stiffness, without an increase in Tan Delta values, or hysteresis, as compared to both Control Sample A to which no clay was added and Control Sample B to which a non-intercalated montmorillonite clay was added.

[0073] This is considered herein to be significant and beneficial because a stiffer rubber (higher modulus value) is observed which is a rubber physical property often desired for various tire components, which was obtained without a significant sacrifice in Tan Delta values which is also a desirable effect for various tire components.

[0074] For Samples C, D and E, the 100 percent and 150 percent modulus values are appreciably increased, as well as the 200 percent moduli for Samples C and E, as compared to Control Samples A and B whereas ultimate tensile strength and ultimate elongation values are only somewhat decreased and for Sample E, the elongation is comparable. The gain in 100 and 150 percent modulus values is more important than loss in ultimate tensile strength.

[0075] This difference in relative gain and loss in such values is considered herein to be an interesting phenomenon which can have beneficial results for rubber compositions for use in various tire components. For example, this is considered herein to be significant because the indicated loss in ultimate tensile strength might be tolerated for various tire components, depending upon the tire component involved, when such large increase in 100 and 150 percent modulus strength is observed.

[0076] For Sample E, it is observed that replacing 15 phr of carbon black with an inclusion of 5 phr of in situ intercalated clay, a greater increase in stiffness (modulus) and ultimate tensile strength values were obtained, together with equal or reduced hysteresis (Tan Delta values) as compared to the values for Sample C which also contained the in situ

intercalated clay but with an inclusion of carbon black comparable to Control Sample A.

[0077] For Control Sample F, with the addition of the pre-intercalated clay instead of the in situ intercalated clay for Samples C, D and E, it is seen that modulus value increased, as expected, as compared to Control Sample A.

[0078] However, interestingly, the modulus values for Sample F did not increase as much as the modulus value for Sample C in which the intercalation of the clay was caused to occur in situ within the elastomer host.

[0079] For Sample F, the indicated ultimate tensile strength value was greater than Control Sample A (without a clay addition) and less than the ultimate tensile strength of Sample C in which the clay was intercalated in situ within the elastomer host.

[0080] Both of these observed physical property observations indicate that a different rubber composition is obtained by causing the clay to intercalate and at least partially exfoliate in situ within the elastomer (Samples C, D and E) as compared to adding a pre-intercalated clay (Control Sample F) or adding the clay without any quaternary ammonium salt treatment (Control Sample B).

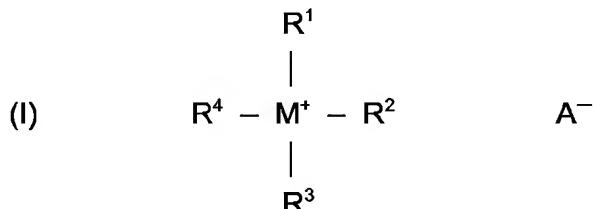
[0081] The aforesaid relative increase in modulus values for Sample C, D and E is considered herein to be significant because higher stiffness (higher modulus value) is usually desirable for various tire components while low hysteresis (e.g. lower Tan Delta value at one percent strain, or elongation) is indicative of lower rolling resistance (improved fuel economy) for a tire having a component (e.g. tread) of such rubber composition.

## Claims

1. A process of preparing a rubber composition which contains a dispersion of intercalated and at least partially exfoliated clay which comprises blending, based upon parts by weight per 100 parts by weight rubber (phr):

- A. 100 phr of at least one hydrocarbon diene-based elastomer,
- B. one to 20 phr of smectite clay,
- C. hydrocarbyl onium salt, and
- D. 20 to 99 phr of at least one additional reinforcing filler comprised of carbon black, synthetic amorphous silica or silica treated carbon black and mixtures thereof,

wherein said hydrocarbyl onium salt is of the general formula (I) represented in an ionized form comprised of a cation and an anion ( $A^-$ ):



wherein  $R^1$  is hydrogen or an alkyl group containing from one to three carbon atoms;  $R^2$ ,  $R^3$  and  $R^4$  are individually selected from alkyl groups having from one to 40 carbon atoms and allyl and aryl groups having from 6 to 40 carbon atoms; and

wherein  $A^-$  is an anion selected from one of chloride, bromide, iodide, fluoride, cyanide, nitrate, hydroxide, thiocyanate, perchlorate, chlorate, bromate, permanganate, formate, acetate, propionate, benzoate, m-toluate, p-toluate, salicylate, methane sulfonate, bisulfate, bicarbonate, dihydrogen phosphate, phenoxide, picrate, methoxide, alkoxide and like anions having a single negative charge, and wherein M is selected from nitrogen, sulfur or phosphorous.

2. The process of claim 1 wherein said  $R^2$ ,  $R^3$  and  $R^4$  are individually selected from at least one of methyl, decyl, octyl, octadecyl, benzyl and ethylhexyl groups, and from tallow and hydrogenated tallow.
3. The process of any of the preceding claims 1 and 2 wherein  $A^-$  is  $Cl^-$  and M is nitrogen.
4. The process of claim 1 wherein  $R^1$  is selected from hydrogen, methyl and ethyl groups;  $R^2$ ,  $R^3$  and  $R^4$  are individ-

ually selected from alkyl groups having from 1 to 18 carbon atoms, M is nitrogen and A<sup>-</sup> is Cl<sup>-</sup> and where said clay is selected from montmorillonite clay and hectorite clay.

5. The process of claim 1 wherein said hydrocarbyl onium salt is a quaternary ammonium salt.
6. The process of claim 1 wherein said hydrocarbyl onium salt is selected from methyl trialkyl ammonium chloride, trimethyl alkyl ammonium chloride, dimethyl dialkyl ammonium chloride, dimethyl alkyl allyl ammonium chloride and dimethyl diallyl ammonium chloride.
10. 7. A rubber composition **characterized by** being prepared by the process of any of the preceding claims 1 through 6.
8. A rubber composition **characterized by** being prepared by the process of any of the preceding claims 1 through 6 wherein said clay is selected from montmorillonite clay and hectorite clay.
15. 9. An article of manufacture having at least one component comprised of the rubber composition of claim 7.
10. A tire having at least one component comprised of the rubber composition of claim 7.

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## EUROPEAN SEARCH REPORT

Application Number

EP 02 10 0739

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
P, A	EP 1 211 283 A (CONTINENTAL AG) 5 June 2002 (2002-06-05) * abstract; claims 1,5-7,9; table 1 * * paragraphs '0001!, '0008!-'0012! * * paragraphs '0017!, '0020!-'0023!, '0034! * & US 0 095 008 A 18 July 2002 (2002-07-18) ---	1-10	C08K3/04 C08K3/34 C08K3/36 C08K9/04 C08K9/06
P, A	EP 1 193 085 A (GOODYEAR TIRE & RUBBER) 3 April 2002 (2002-04-03) * abstract; claim 1 * * paragraphs '0029!, '0033!, '0038!-'0042! * ---	1-10	
E	GB 2 370 280 A (GOODYEAR TIRE & RUBBER) 26 June 2002 (2002-06-26) * abstract; claims 1,8,11-13,19-22 * * page 2, line 19 - line 26 * * page 9, line 8 - line 17 * * page 10, line 20 - page 11, line 33 * * page 16, line 13-26 *	1-10	
A	US 6 034 164 A (ELSPASS CHESTER W ET AL) 7 March 2000 (2000-03-07) * abstract; claim 1; examples 1,2 * * column 1, line 60 - line 67 * * column 2, line 8 - line 9 * * column 2, line 34 - line 42 * * column 3, line 15,21 - line 35 * ---	1-10	<div style="border: 1px solid black; padding: 2px;">TECHNICAL FIELDS SEARCHED (Int.Cl.)</div> C08K C08L
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	19 September 2002	Schütte, M	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 10 0739

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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19-09-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1211283	A	05-06-2002	DE EP JP US	10059236 A1 1211283 A1 2002179842 A 2002095008 A1	20-06-2002 05-06-2002 26-06-2002 18-07-2002
EP 1193085	A	03-04-2002	BR EP JP	0104162 A 1193085 A2 2002160504 A	07-05-2002 03-04-2002 04-06-2002
GB 2370280	A	26-06-2002	BR JP	0105083 A 2002167475 A	25-06-2002 11-06-2002
US 6034164	A	07-03-2000		NONE	